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Comparison of thermal analysis and differential thermal analysis for evaluating solid fraction evolution during solidification of Al-Si alloys.

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Abstract. Both thermal analysis (TA) and differential thermal analysis (DTA) have been used since long to evaluate latent heat release and solid fraction evolution during solidification of metallic alloys. TA makes use of cooling curves recorded under "natural" cooling while DTA consists in recording the temperature difference between the sample temperature and an inert reference during a controlled cooling, i.e. at imposed constant cooling rate. In both cases, the solid fraction evolution is deduced from a calculation of the latent heat release as estimated by means of a heat transfer model. This paper provides a comparison of such evaluations performed on one Al-Si alloy.

Introduction

Latent heat release and solid fraction evolution during solidification of metallic alloys are usually evaluated by techniques such as thermal analysis (TA) and differential thermal analysis (DTA). TA is essentially performed on standard cups filled with liquid on cast-shop floor and allowed to cool under air. Such records are used for quality control of melt preparation. DTA is instead a laboratory facility, it consists in recording the temperature difference between a sample and an inert reference during controlled cooling, i.e. at imposed cooling rate, and involves generally very small quantity of material.

The aim of the present work was to compare the solid fraction evolution as evaluated from TA and DTA in the case of an Al-Si alloy. TA records from standard cups were analyzed using the so-called Newton-like heat exchange model. A new method is proposed to determine the zero line, i.e. the cooling schedule that the TA sample would follow if there were no phase change [1]. The appropriateness of the method has been checked by comparing the latent heat evaluated from this analysis to the value predicted by means of thermodynamic calculations. DTA records were analyzed using the heat transfer model proposed by Boettinger and Kattner [2] after proper calibration of the model parameters with pure aluminium samples. Again, the model gives estimate of the latent heat released during solidification that can be compared to other values. Finally, integrating and normalizing the heat release versus time gives estimate of the evolution of the solid fraction that can be plotted against prediction made with the Scheil's model.

Experimental details

The alloy used for the present study is an AS7G alloy, its composition is listed in Table 1. Before casting, a eutectic modifier is added to the melt that could be either strontium or sodium. From the whole series of experiments detailed elsewhere [1], only the two records performed with the Sr modified alloy will be presented here. Digital records of the cooling curves were obtained by means of the Thermolan-Al system [3]. The DTA samples were machined out from the TA cups and the experiments were performed with a SETSYS facility from SETARAM. Calibration of the cell showed it gives temperatures too low by three degrees, and all the DTA records have been corrected accordingly. By extrapolating to a zero scanning rate the characteristics temperatures observed on DTA records performed at various scanning rates, the liquidus of the alloy was estimated at 612°C and the temperature for solidification completion at 554°C [1].

Si	Fe	Cu	Mn	Mg	Zn	Ti	Sr
6.84	0.08	<0.01	<0.01	0.54	0.03	0.14	0.024

Table 1 – Composition (wt. %) of the AS7G alloy used in this work.

Results

In Fig. 1 are plotted the cooling curves recorded with the two standard cups, where it is seen that the overall solidification time differs slightly from one record to the other although much care was taken to ensure reproducible filling conditions. This slight difference may be partly due to the change in casting temperature and partly to some variation of the weight of metal poured in the cup. Three thermal arrests are easily noticed on both cooling curves: i) the onset of solidification when (Al) dendrites start forming; ii) the beginning of the bulk (Al)-Si eutectic and iii) a slightly less pronounced arrest towards the end of the eutectic plateau when minor phases precipitate. Also shown is the cooling rate corresponding to the curve with the longer solidification time that has been obtained by differentiating the recorded data and then smoothing (central average on 10 measurements). Each of the three thermal arrests is associated to a peak on this latter curve. Note that the two nearly vertical lines are due to physical noise during recording. At the end of the eutectic plateau, the cooling rate decreases abruptly though it does not seem easy to ascertain when solidification stops effectively.

It was decided to rely on the Newton-like method to analyze the cooling curves. Following the lines described by Chen and Stefanescu [4], the heat balance is given as:

$$-h.A.(T - T^\circ) = V.\rho.C_p.\frac{dT}{dt} + \frac{dQ_L}{dt} \quad (1)$$

where V and A are the volume and the outer area of the cup, ρ and C_p are the specific mass and the specific heat of the material, h is the Newtonian heat transfer coefficient, T and T° are the temperature of the material and the outer temperature, and Q_L is the latent heat released by the sample because of solidification which is defined as a negative quantity.

It was observed that the h coefficients, that allow to fit the heat transfer conditions during cooling before and after solidification, greatly differ between each other. This is illustrated in Fig. 2-a where has been plotted again one of the previous cooling curves and its derivative (with solid lines), and the calculated cooling curves before and after solidification (in interrupted lines), fitted with the cooling rate at 635°C and 540°C respectively. The dotted lines show the derivatives of these latter curves, and it is seen that they could hardly be adjusted one to each other. This shows that the heat exchange conditions change drastically during solidification, e.g. because of metal shrinkage during solidification of the cup leading to the formation of an air gap between the metal and the cup.

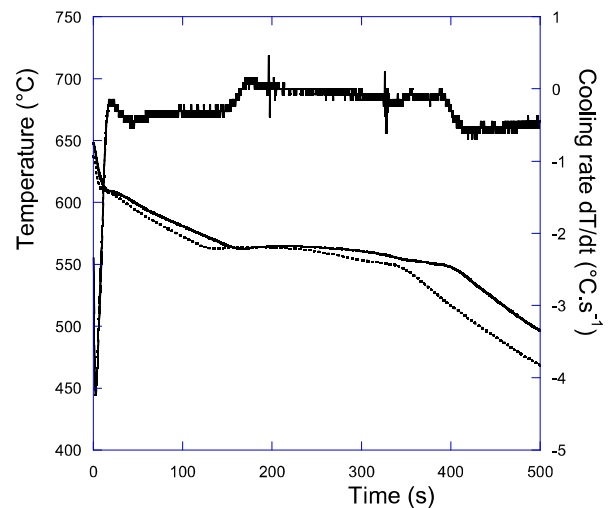


Figure 1 – Temperature-time curves recorded by standard TA analysis, and time derivative of the curve showed with solid line.

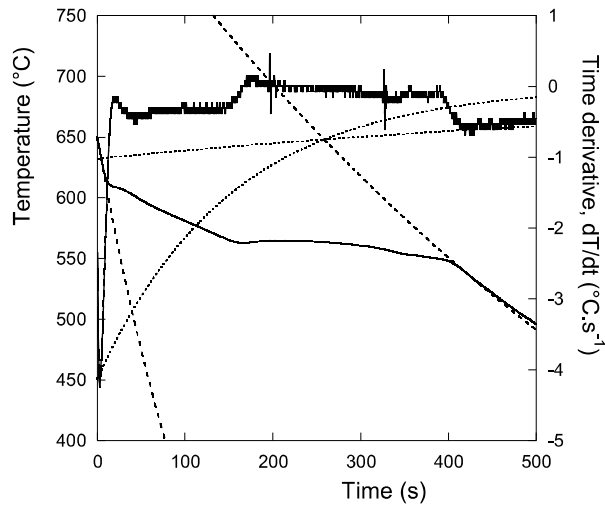


Figure 2 (a) - Examples of one experimental cooling curve and its derivative (solid lines) and the two reference curves for cooling without phase change (interrupted lines) calculated above the liquidus and below the solidus. The derivatives of these latter curves are also drawn with dotted lines.

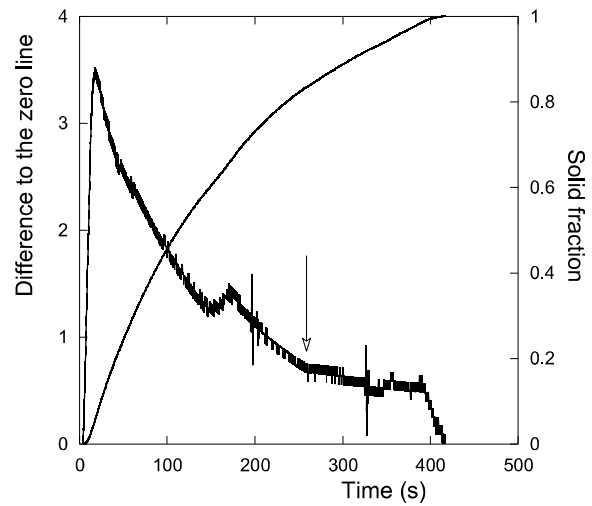


Figure 2 (b) – Time evolution of: i) the difference between the experimental derivative of the cooling curve and the base line; and ii) the solid fraction obtained by integrating and normalizing the difference curve. The arrow shows the time at which the selected base line was switched from the high temperature to the low temperature one.

This suggested defining the base line, i.e. the so-called zero line that the sample should follow if there were no phase change, as given at any time by the lower of the two calculated derivative curves. Once the base line thus defined, the heat released during the solidification step is given by the difference between the experimental cooling rate curve (time-derivative of the cooling curve) and the zero line. Fig. 2-b shows the plot of this quantity for the curve in Fig. 2-a. The location for the change of base-line is indicated with the arrow, and it is seen it does not lead to any significant effect on the calculated heat release curve. Finally, assuming that the latent heat of solidification per unit volume does not change from primary to eutectic solidification, this curve may be integrated and normalized to give an estimate of the solid fraction evolution. The calculation is also presented in Fig. 2-b.

The estimated evolution of the solid fraction may be conveniently plotted versus temperature. Fig. 3 compares the curves thus obtained from the two cooling curves showed in Fig. 1. It is seen that, though the cooling curves presented some discrepancies, the solid fraction evolution plotted in that way is highly reproducible. The conditions for achieving such reproducible results have been verified and discussed on the basis of a much larger set of records [1].

It may be noted however on the curves in Fig. 3 that there is an apparent slow increase of the solid fraction before the actual onset of solidification. This is an artefact linked to the choice of the reference temperature considered for simulating high temperature cooling, and this artefact could be avoided by selecting a start temperature closer to the actual liquidus temperature of the alloy. The discrepancy thus induced is in fact very limited and was not considered as having any relevance in the present work. It could be easily possible to renormalize the curve by considering that the actual start of solidification relates to a slope of the curve higher than a minimum threshold value.

Modeling of DTA followed the work by Boettinger and Kattner [2] in which a description of heat exchanges between the sample, crucible, thermocouple and furnace wall allows reproducing the main features of DTA records. According to these authors, three heat balance equations could be written for the sample side [2]:

$$m_s.C_p^s.\frac{dT_s}{dt} + \frac{dQ_L}{dt} = \frac{m_c.C_p^c}{\tau_{sc}}.(T_c - T_s) \quad (2)$$

$$\frac{dT_c}{dt} = \frac{1}{\tau_{sc}}.(T_s - T_c) + \frac{1}{\tau_{wc}}.(T_w - T_c) + \frac{1}{\tau_{sr}}.(T_{cr} - T_c) \quad (3)$$

$$\frac{dT_T}{dt} = \frac{1}{\tau_{TC}}.(T_c - T_T) \quad (4)$$

where m_s and C_p^s are sample weight and heat capacity, m_c and C_p^c are crucible weight and heat capacity, T_s , T_c , T_T and T_w are sample, crucible, sample thermocouple and furnace temperatures respectively, τ_{sc} , τ_{wc} and τ_{TC} are time constants that characterize heat exchanges between sample and crucible, furnace and crucible, and thermocouple and crucible respectively. The last term in the right hand side of Eq. 3 has been added with respect to the simplified model considered by Boettinger and Kattner [2], it describes heat exchange between sample cup at T_c and reference cup at T_{cr} , with τ_{sr} the corresponding time constant.

Note that the whole left hand side of equation (2) should be better written ($m_s.dH/dt$) with H the enthalpy of the material, but considering separately heat capacity and latent heat does not have any practical effect on the calculations in the case of Al-Si alloys while being much easier to handle.

Boettinger and Kattner [2] simulated DTA records using heat evolution with temperature that was calculated by other means, e.g. thermodynamic calculations, and then compared them to experimental records. In the present work, a reversed calculation was performed to get solidification kinetics from experimental DTA records. These records are obtained as files listing time, the temperature of the sample thermocouple T_T and the DTA signal $\Delta T = T_T - T_{TR}$ where T_{TR} is the temperature given by the reference thermocouple. As ΔT is in fact equal to $T_T - T_w$ up to a constant [2], it was decided to subtract the base line from the DTA records and calculate only the part of the DTA signal that is due to latent heat release. Further, the term $(T_{cr} - T_c)$ in Eq. 2 was replaced by ΔT as it should be at any time very close to that value.

The above set of equations has been solved with an explicit numerical scheme and the time constants were evaluated by trial and error on melting and solidification of pure aluminium samples of various heights and thus weights. The mass of every sample was measured before DTA runs and C_p was fixed at $917 \text{ J.K}^{-1}.\text{kg}^{-1}$. A convenient set of parameters was found to be $\tau_{sc}=13 \text{ s}$, $\tau_{wc}=3 \text{ s}$, $\tau_{TC}=17 \text{ s}$, $\tau_{sr}=8 \text{ s}$ and $m_c.C_p^c=0.15 \text{ J.K}^{-1}$.

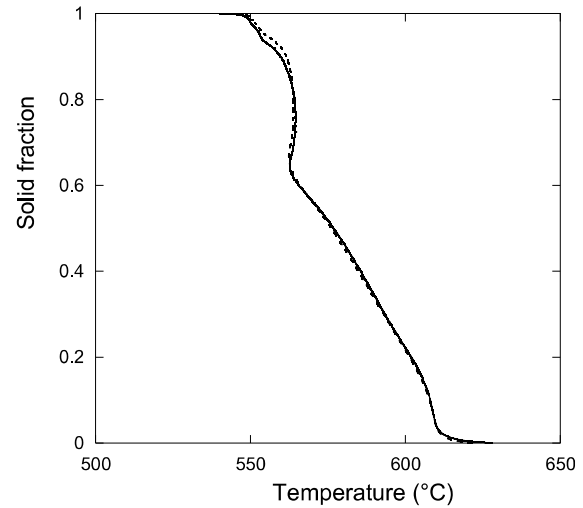


Figure 3 – Evolution of the solid fraction as estimated from the two cooling records of Fig. 1.

The capability of the method was then checked on a binary Al-Si alloy. Fig. 4-a shows with full lines the measured T_T and ΔT values during cooling at $5 \text{ K} \cdot \text{min}^{-1}$ of a sample (190 mg in weight), and with dotted lines the calculated sample temperature T_S and the instantaneous heat evolved during solidification $\delta(Q_L)$. The DTA signal shows two peaks related to precipitation of (Al) and of the (Al)-Si eutectic respectively. Both reactions are associated with a very sharp increase of ΔT at the beginning of the corresponding thermal arrest. As a matter of fact, the calculated T_S curve shows that the sample did present recalescence at the start of these two reactions though this does not appear on the experimental T_T record.

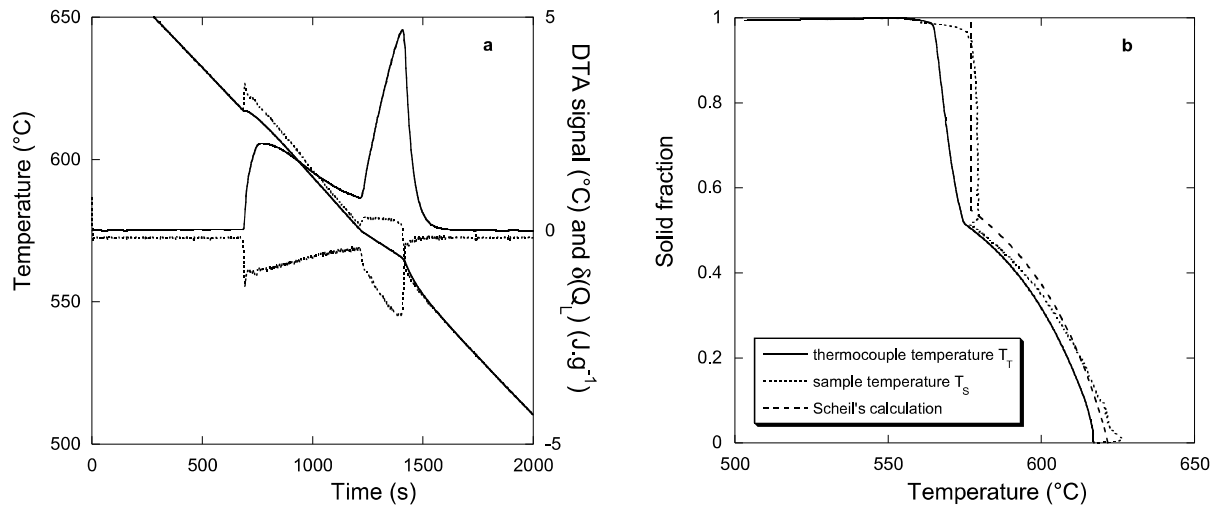


Figure 4 – (a) Reverse calculation applied to solidification at 5 K/min of an Al-Si alloy; the calculated T_S and $\delta(Q_L)$ values are showed with dotted lines while the input T_T and ΔT curves are in solid lines.

(b) calculated solidification kinetics plotted versus recorded T_T (solid line) and calculated T_S (dotted line) as compared to prediction from the Scheil's model (interrupted line).

In figure 4-b is shown the calculated evolution of the solid fraction plotted versus the recorded thermocouple temperature (solid line) and the calculated sample temperature (dotted line). As expected, the eutectic reaction appears nearly isothermal when plotted versus the sample temperature T_S , whilst this is not the case on a usual DTA record (ΔT , T_T). In the figure has been plotted also the evolution of the solid fraction as evaluated by means of the Scheil's module of Thermocalc [5] using the COST-2 databank for light alloys [6], for an alloy with 6.2 wt. % Si. A quite reasonable agreement is obtained between this evaluation and the calculation performed in the present work, apart for the very end of the eutectic reaction. This discrepancy relates to the fact that the latent heat release does not drop to zero abruptly at the end of the eutectic plateau but reaches this value only after some time. This feature seems to be unfortunately an inherent limit of the DTA model, though it could possibly be improved by use of an implicit numerical scheme.

DTA experiments were finally performed with 80 mg samples of the AS7G alloy cooled at 5 , 10 , 15 and $20 \text{ K} \cdot \text{min}^{-1}$, and the solidification kinetics were calculated and are reproduced in Fig. 5-a. Both primary deposition and eutectic reaction are shifted to decreasing temperature with increase of the cooling rate. While this feature was expected for the eutectic reaction, it is somehow astonishing for the primary deposition as the cooling rates investigated are quite low. This is tentatively related to the fact that very small samples were used. It is also noted that solidification ends at a temperature which is sensitive to the cooling rate, a feature that can be related again to the above mentioned limit of the present modelling.

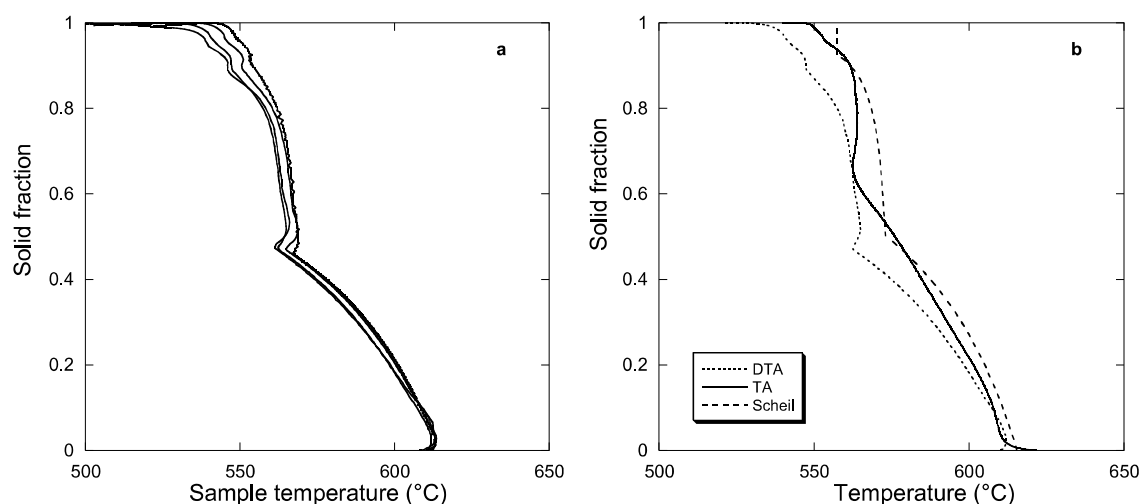


Figure 5 – (a) Solidification kinetics calculated from DTA records at increasing cooling rate (5, 10, 15 and 20 K.min⁻¹) on AS7G samples; (b) comparison of the solidification kinetics estimated from TA and DTA (15 K.min⁻¹) as compared to thermodynamic prediction.

Discussion and conclusion

Solidification kinetics as estimated from TA and DTA are compared in Fig. 5-b where has been reported also the curve calculated with the Scheil's module of Thermocalc. It is seen that there is a quite reasonable agreement between the different curves for primary deposition of (Al), though TA seems to overestimate and DTA to underestimate the solid fraction at the start of the eutectic reaction. As expected, the (Al)-Si eutectic reaction appears experimentally significantly undercooled. Latent heat values estimated from TA and DTA were found to be within less than 10 % of the theoretical value as given by the COST-507 database for a solidification following the Scheil's model. This supports the overall heat exchange modelling approaches employed.

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